

CHEMICAL FACTOR IN LIQUID-RECRYSTALLIZATION SINTERING OF CORUNDUM

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Sintering of corundum according to the liquid-recrystallization mechanism is studied by introducing borosilicate additives of eutectic compositions. The comparative efficiency of flux-forming additives is determined. The structure of melts is studied. The chemical factor affecting sintering is identified and relations for the qualitative estimate of this factor are proposed.

Sintering is the most important process in the technology of ceramics and powder metallurgy occurring under high-temperature treatment (firing) of porous compacts. The initially porous compacts as a consequence of sintering become dense and acquire strength.

The motive force of sintering is the excessive surface energy of disperse particles on the phase interface. If sintering occurs in a solid – liquid – gaseous system, it is called liquid-phase sintering. The more common and preferable version of this process is where the liquid phase dissolves solid particles (reacts with them).

Credit for theoretical interpretation of sintering in the presence of a liquid phase reacting with the solid phase goes to Kingery [1]. He was the first to substantiate the possibility of complete densification of porous compacts in the presence of small (below 35 vol.%) quantities of liquid. In this case sintering does not stop at the moment of the maximum approach of solid particles, since the contact sites start dissolving and the centers of particles approach even closer to each other. As a consequence, the volumetric content of crystalline phases in material reaches 80–90% instead of 60–65%, which is the maximum possible content when the melt does not dissolve solid particles.

According to Kingery's theory, a prerequisite of sintering is the perfect wetting of solid particles and the penetration of liquid between these particles. As the result of the contracting effect of capillary forces, the system in sintering experiences a pressure equivalent to a certain hydrostatic pressure applied to the whole system. The pressure at the points of contacts between solid particles divided by thin liquid interlayers is higher than the average hydrostatic pressure applied to the whole system. This increases the chemical potential (activity) of the sintered material at the contact points.

Kingery derived the following relationship to describe the process kinetics at the stage called the “dissolution – precipitation (crystallization) stage”:

$$\frac{\Delta l}{l_0} = \frac{1}{3} \frac{\Delta V}{V_0} = \left(\frac{6k_2 \delta D C_0 \gamma V_m}{k_1 R T} \right)^{1/3} r^{-4/3} t^{1/3}, \quad (1)$$

where $\Delta l/l_0$ and $\Delta V/V_0$ is the relative decrease in the length and volume of the sample, respectively; k_1 and k_2 are geometric constants; δ is the thickness of the liquid film between the solid particles; D is the diffusion coefficient; C_0 is the solubility of the solid phase in the liquid; γ is the surface tension at the liquid – gas interface; V_m is the molar volume of the solid phase being dissolved; R is the gas constant; T is the absolute temperature; r is the initial radius of particles; t is the process duration.

Relation (1) is applicable to spherical particles under the diffusion control of the material transfer velocity. Particles in many systems demonstrate a clearly expressed prismatic habitus. They may contact each other with flat surfaces or edges. For this case Kingery derived analogous formulas with other geometrical constants.

Kingery and Narasimhan [2] experimentally investigated the effect of various factors on sintering in the Fe – Cu system, such as process duration, initial size (radius) of solid particles, and temperature, which enter the theoretical formula (1) as variables or parameters, as well as the effect of the quantity of melt. The experiments corroborated the theoretical assumption of Kingery that it is possible to reach full sintering when the solid phase does not dissolve in the liquid one, provided the system contains at least 35 vol.% melt.

Kukolev investigated the sintering of corundum reacting with an estimated quantity of melt depending on its composition for the systems $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$, $\text{MgO} - \text{Al}_2\text{O}_3 -$

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TABLE 1

Number of borosili- cate additive	Eutectic melting tem- perature, °C	MeO	Molar content, %		
			MeO	B ₂ O ₃	SiO ₂
1	1270	MgO	70	26	4
2	950	BaO	31	28	41
3	810	BaO	22	67	11
4	977	CaO	42	28	30
5	1118	CaO	62	14	24

SiO₂, Na₂O – Al₂O₃ – SiO₂, and K₂O – Al₂O₃ – SiO₂. It was established that the optimum sintering is observed when the points of the melt composition lie within the field of the primary crystallization of corundum, and the poorest sintering is seen when the points lie on the mullite – corundum curve. The obtained data are interpreted in the context of the theory of structure of melts. When a melt is at equilibrium only with the phase under sintering (corundum), it contains only octahedrally coordinated aluminum ions, same as in corundum, which facilitates sintering [3]. Kukolev believes that the critical factor facilitating sintering is the presence in the melt of a large number of groups whose structure (to a certain extent) corresponds to the structure of the solid phase being sintered [4]. Here we deal with so-called sybotaxic groups. The latter are pseudocrystalline aggregates present in the melt whose structure approaches the structure of the respective crystals formed in crystallization of the liquid [5].

Appen [6] proposed simple relations enabling one to easily determine the coordination of aluminum and boron ions in glass. If a glass contains alkali metal oxides and does not contain boron, then, with a molar ratio of Me₂O : Al₂O₃ equal to 1, all aluminum ions are tetrahedra AlO₄. If the specified ratio is less than 1, then part of aluminum ions transform into octahedra AlO₆. In the general case one can judge the coordination of aluminum and boron ions based on the dimensionless parameters ψ_{Al} and ψ_B :

$$\psi_{Al} = (Me_2O + k MeO)/Al_2O_3; \quad (2)$$

$$\psi_B = (Me_2O + k MeO - Al_2O_3)/B_2O_3, \quad (3)$$

where M₂O, MeO, Al₂O₃, and B₂O₃ are molar parts of the oxides of alkali, alkaline-earth metals, aluminum, and boron, respectively, and k is the activity coefficient.

Strictly speaking, Appen did not specify the activity coefficient in these formulas, although he mentioned that the activity of BaO is the same as that of Na₂O. Active oxides include Na₂O, K₂O, and BaO. Less active are Li₂O, SrO, and CaO.

Aluminum is the first to pass to the tetrahedral coordination, and boron does that afterwards. In the case of a deficit of Me₂O and MeO in the melt, aluminum is capable of transforming boron into the three-coordination state BO₃, meanwhile acquiring the tetrahedral coordination AlO₄.

The purpose of the present paper is to achieve full sintering of corundum ceramics under a temperature not higher than 1500°C and to analyze this process in correlation with the melt structure. This study has a practical purpose, since the common varieties of corundum ceramics containing fluxes have a substantial disadvantage: a high (1600 – 1650°C) sintering temperature. The study was based on the principle of lowering the sintering temperature, namely, introducing various additives (fluxes) in mixtures. Considering that the firing temperature should be no higher than 1500°C, the temperature of the emergence of the liquid phase, accordingly, should be even lower.

Departing from this assumption and using the known phase diagrams [7], eutectic compositions in the ternary systems MeO – B₂O₃ – SiO₂ were selected as additives, where MeO is MgO, CaO, or BaO (Table 1).

According to the data of Andrianov, et al. [8], a complete moistening of a polycrystalline corundum plate by eutectic borosilicate melts takes place at a temperature not higher than 1300°C. Thus, moistening as a prerequisite of sintering poses is ensured.

For better understanding of the processes occurring in sintering of corundum, model glasses have been synthesized and investigated. The authors departed from the classical concept of glass as a supercooled liquid retaining the specifics of its melt structure. The glass melting temperature was selected equal to the temperature of firing ceramics.

The raw material was alumina GLMK containing 0.2 – 0.3 wt.% MgO (TU 48-5-88-85). The study of the phase composition indicates that this alumina contains (vol.-%): 97% α -Al₂O₃ with particle size of 1 – 4 μ m, 2% alumomagnesian spinel, and 1% impurity in the form of a vitreous phase.

The additives were introduced in the amount of 5, 10, and 20 wt.% in the form of glasses melted at 1450°C. Samples were molded of mixtures prepared by moist mixing with a binder containing 70 vol.% of 10% PVA solution and 30% glycerin, under a pressure of 100 – 125 MPa. Firing was carried out in a furnace with chromite-lanthanum heaters. The average heating rate was 200 K/h, and the exposure at the final temperature was 2 h. The temperature was monitored with an optical pyrometer. Samples in firing were held in a closed crucible to prevent changes in their chemical composition. Sintering was investigated by the method of successive firings in the temperature interval of 1450 – 1550°C. The degree of sintering was estimated based on water absorption, open porosity, and apparent density. These parameters were determined by the saturation, and hydrostatic weighing methods (GOST 2409-80). The samples were weighed on an analytical scale with an accuracy of 0.0001 g. The experiments were performed simultaneously on 5 samples. Moreover, a continuous shrinkage of samples in firing was studied using a BeO dilatometer under a heating rate of 10 K/min in air. Combining the dilatometer with a computer made it possible to register continuous shrinkage and its rate.

This experiments was performed for samples with equal weight content of additives (10%).

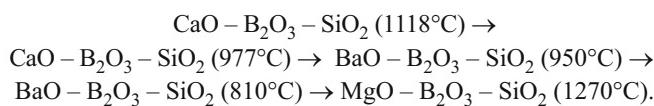
Model glasses were melted in corundum crucibles at 1450°C. After a 1-h exposure the melts were discharged on a thick steel plate.

The IR transmission spectra of model glasses were registered using a Specord-M80 two-ray spectrophotometer in the wave number range of 400 – 2000 cm⁻¹. Samples were prepared by joint molding of fine powder with anhydrous potassium bromide according to the standard procedure. Characteristic groups were identified based on published data [9 – 14].

The poorest sintering results were obtained using flux of the MgO – B₂O₃ – SiO₂ system. Even the introduction of 20 wt.% of this flux does not ensure a dense (pore-free) material, whereas any other flux makes that possible (Table 2).

The optimum results in sintering alumina were obtained with a flux of the CaO – B₂O₃ – SiO₂ system (Tables 1 and 2, mixture 5). The introduction of 5 and 10 wt.% of this flux makes it possible to produce ceramics with zero water absorption at the temperatures of 1550 and 1450°C, respectively. The fact that the introduction of such small quantities of flux results in perfect densification leaves no doubt that sintering occurs by the dissolution – crystallization mechanism. The content of 5 – 7% flux-forming additive is typical of corundum materials produced in the domestic industry [VK94-1 (22KhS), VK94-2 (M-7), etc.] sintering at the temperature of 1600 – 1650°C according to the specified mechanism.

Fluxes based on the considered systems can be ranked in the order of decreasing efficiency (eutectics melting temperatures are indicated in brackets):



The highest shrinkage in the interval of 700 – 1500°C is registered in samples with the flux of the system CaO – B₂O₃ – SiO₂ (1118°C). The ranking of continuous shrinkage curves of samples depending on the type of additives agrees with the above sequence of relative flux efficiency, and the shrinkage rates have clearly defined maxima (Fig. 1). The maximum for the flux of the CaO – B₂O₃ – SiO₂ system (1118°C) is 1300°C, and for the flux of the CaO – B₂O₃ – SiO₂ system (977°C) it is 1400°C; for fluxes of BaO – B₂O₃ – SiO₂ (950°C) and BaO – B₂O₃ – SiO₂ (810°C) systems the shrinkage rate coincides in the whole temperature range and its maximum corresponds to 1460°C. Obviously, the most efficient flux corresponds to the lowest temperature at which the maximum shrinkage rate is achieved.

All ternary borosilicate systems used as sintering additives form clear glasses without signs of crystallization, liquation, or insufficient melting, which was experimentally demonstrated. This suggests that melt compositions are iden-

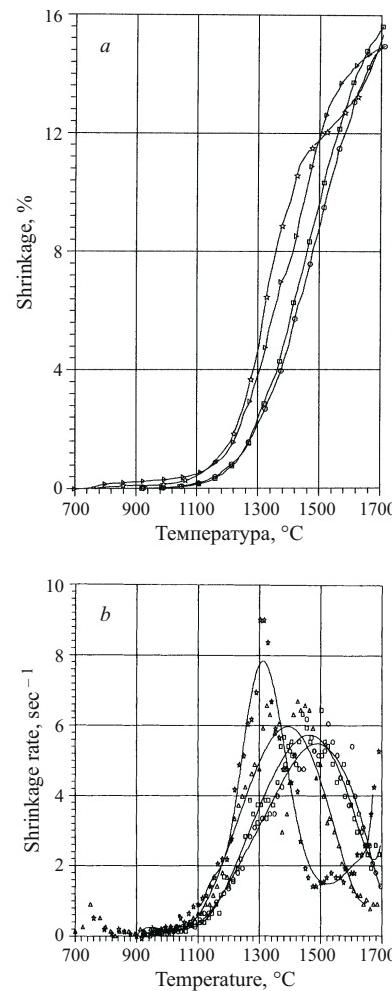


Fig. 1. Continuous shrinkage (*a*) and its rate (*b*) for samples of Al₂O₃ containing 10% borosilicate additive (see the additive composition in Table 1): □, ○, △, and ★) additives 2, 3, 4, and 5, respectively.

TABLE 2

number in Table 1	Additive used	Properties of alumina samples			
		weight content, %	firing temperature, °C	water absorption, %	apparent density, g/cm ³
1	5	1550	9.12	2.74	27.0
	10	1550	5.00	2.85	20.0
	20	1550	3.70	2.96	16.0
2	5	1550	8.75	2.90	24.0
	10	1450	1.23	3.40	4.7
	20	1450	0.00	3.46	0.0
3	5	1550	8.78	2.85	25.4
	10	1450	1.90	3.37	6.4
	20	1450	0.00	3.44	0.0
4	5	1550	3.94	3.01	13.2
	10	1450	0.01	3.49	0.1
	20	1450	0.00	3.51	0.0
5	5	1550	0.00	3.65	0.0
	10	1450	0.00	3.70	0.0
	20	1450	0.00	3.52	0.0

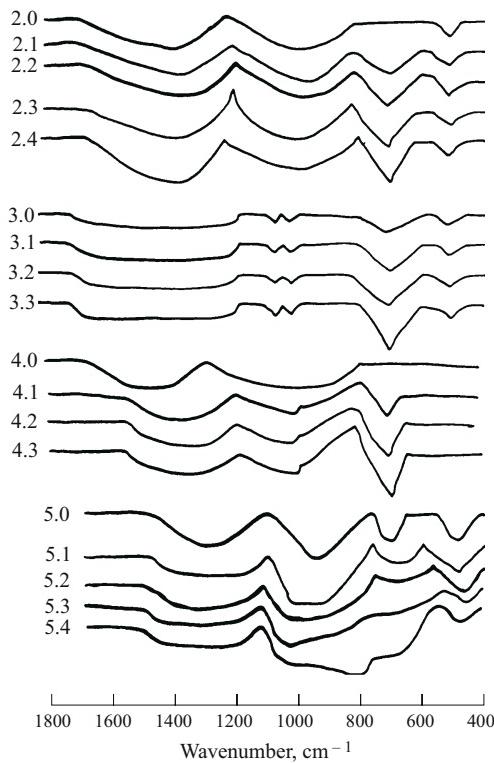


Fig. 2. IR spectra of model glasses. Curve numbers correspond to mixture numbers.

tical to glass compositions. An exception is the $\text{MgO} - \text{B}_2\text{O}_3 - \text{SiO}_2$ system (1270°C), which does not form clear glass and is excluded from further consideration.

In order to estimate the maximum possible content of alumina in the melt, i.e., its solubility, we synthesized model glasses adding alumina portions to the batch until it stopped dissolving or until the emergence of crystallization symptoms. For convenience, model glasses are grouped into series. Within the same series the same sintering additive is used (Table 1); the first digit of the model glass number corresponds to the number of the additive. Model glass compositions with index “0”, i.e. 2.0, 3.0, 4.0, and 5.0 (Table 3) do not contain alumina and coincide with the compositions of sintering additives 2, 3, 4, and 5 (Table 1).

A specific feature of model glasses without alumina is their propensity for destruction when cooled after melting. The destruction occurs under the effect of internal stresses. The most intense destruction occurred in glass 5.0; it fractured into small fragments interspersed by numerous cracks. Other glasses not containing alumina are also prone to destruction, but the less so, the less alkaline-earth oxide they contain. The introduction even of the first portion of alumina significantly delays destruction; as the content of alumina increases, the destruction stops altogether.

As the content of alumina in glass increases, the degree of covalent cohesion of its structure grows, i.e., the introduced aluminum oxide acts as a glass-forming agent incorporating into the silicon-oxygen pattern of glass. It is known

that aluminum can incorporate into the silicon-oxygen pattern only in the tetrahedral coordination with respect to oxygen [6]. For aluminum to act as a glass-forming agent, the glass should have a high content of alkali and alkaline-earth oxides and a low content of silica. In this case AlO_4 groups presumably displace BO_4 group from the silicon-oxygen pattern, transforming them into BO_3 groups. Thus, a preliminary conclusion can be made that alumina introduced into glass mainly transforms into AlO_4 and not into AlO_6 . Such conclusion disagrees with the statement of Kukolev [3, 4] that sintering improves if AlO_6 groups rather than AlO_4 groups are present in the melt.

In order to verify the coordination of aluminum atoms in glasses, we investigated their IR spectra. According to the published data, the presence of bands in the high-frequency range of $1500 - 1100 \text{ cm}^{-1}$ and in the range of $700 - 600 \text{ cm}^{-1}$ is an indication of three-coordination boron, whereas the range of $1000 - 900 \text{ cm}^{-1}$ is more typical of four-coordination boron [9 – 11]. The latter range also covers the main range of stretching vibrations of silicon-oxygen links ($1100 - 900 \text{ cm}^{-1}$) [12, 13]. The coordination state of boron is relevant, since it is known [6] that in the case of a shortage of oxygen supplied to the melt via alkaline-earth oxides for the construction of AlO_4 tetrahedra, aluminum is capable of taking oxygen from boron, thus transforming it into the three-coordination state.

The vibrations of aluminum-oxygen links depending on the degree of polymerization are manifested in the ranges of $870 - 650 \text{ cm}^{-1}$ for groups AlO_4 and $650 - 400 \text{ cm}^{-1}$ for groups AlO_6 [12 – 14].

The identification of characteristic groups in model glasses based on their IR spectra (Fig. 2) did not register the presence of octahedra AlO_6 . The presence of a band with an extremum at 450 cm^{-1} in glasses of series II cannot be regarded as an indication of AlO_6 , since this band is also present in the spectrum of glass not containing alumina (Fig. 2, mixture 2.0). Furthermore, the intensity of this band does not change as Al_2O_3 content grows.

The main conclusion ensuing from the analysis of IR spectra of model glasses is that alumina introduced in glass batches passes to the tetrahedral state in all glasses. This is accompanied by the transition of boron into the three-coordination state, except for the glasses of series V where all boron remains four-coordination, which is another confirmation of the transition of aluminum to AlO_4 and not to AlO_6 .

Thus, the results of studying IR spectra agree well with the increasing covalent cohesion of glass structure observed upon introducing alumina. However, the obtained experimental data do not agree with the known concepts of Kukolev [3, 4] on a correlation between sintering and the melt structure, since fluxes of the $\text{CaO} - \text{B}_2\text{O}_3 - \text{SiO}_2$ system effectively facilitate sintering, despite the absence of AlO_6 groups.

Let us identify criteria that could relate the chemical composition and the melt structure to the sintering results. The most suitable for this purpose are two criteria used in

TABLE 3

Series	Model glass		Content, molar parts					Ratio MeO : Al ₂ O ₃	ψ_B
	number	based on sintering additive	Al ₂ O ₃	BaO	CaO	B ₂ O ₃	SiO ₂		
II	2.0	2	—	0.31	—	0.28	0.41	—	1.10
	2.1		0.05	0.29	—	0.27	0.39	5.80	0.88
	2.2		0.10	0.28	—	0.25	0.37	2.80	0.72
	2.3		0.20	0.25	—	0.22	0.33	1.25	0.22
	2.4		0.30	0.21	—	0.20	0.29	0.70	—0.45
III	3.0	3	—	0.22	—	0.67	0.11	—	0.32
	3.1		0.05	0.21	—	0.64	0.10	4.20	0.15
	3.2		0.10	0.20	—	0.60	0.10	2.00	0.06
	3.3		0.20	0.17	—	0.54	0.09	0.85	—0.15
IV	4.0	4	—	—	0.42	0.28	0.30	—	1.05
	4.1		0.05	—	0.40	0.27	0.28	8.00	0.85
	4.2		0.10	—	0.38	0.25	0.27	3.80	0.66
	4.3		0.20	—	0.34	0.22	0.24	1.70	0.17
V	5.0	5	—	—	0.62	0.14	0.24	—	3.10
	5.1		0.05	—	0.59	0.13	0.23	11.80	2.80
	5.2		0.10	—	0.56	0.13	0.21	5.60	2.25
	5.3		0.20	—	0.50	0.11	0.19	2.50	1.36
	5.4		0.30	—	0.43	0.10	0.17	1.43	0.01

glass technology. These are relations (2) and (3) presented above. We are not taking into account the activity coefficient in relation (2) for ψ_{Al} . Then, in the absence of alkali oxides, which is our case, the relation takes the form of MeO : Al₂O₃ ratio. In relation (3) we will accept the activity coefficient for ψ_B equal to 1.0 for BaO and 0.7 for CaO.

For glasses not containing alumina and coinciding in their composition with sintering additives, the relationship of the parameter ψ_B with sintering is obvious: the higher this index, the higher the efficiency of the sintering additive (Table 3). As glasses become saturated with alumina, both parameters decrease, but this decrease is lower the higher the effect of the additive. Hence it can be concluded that the chemical composition of a melt has a greater effect on alumina sintering, than its structure.

To find the limiting values of MeO : Al₂O₃ and ψ_B under which sintered materials can be produced, we investigated the sintering of alumina with model glass additives 5.1, 5.2, 5.3, and 5.4 containing alumina (Table 3). The quantity of alumina in ceramic mixtures was reduced by a quantity equal to its content in the model glass additive. At the same time, the total weight content of alumina was equal in all samples (90%) and the total content of CaO, B₂O₃, and SiO₂ was equal to 10%. The sintering parameters of samples with additive 5.1 containing 0.05 molar parts of Al₂O₃ (Table 4) are nearly identical to those of additive 5 (Table 2). As the content of Al₂O₃ in the additive grows, the sintering parameters deteriorate. When the Al₂O₃ content exceeds 0.1 molar parts, the samples exhibit open porosity. The values of the ratio MeO : A₂O₃ = 5.60 and ψ_B equal to 2.25 are close to the limiting values, when the additive introduced initially contains around 0.1 molar parts of Al₂O₃ [15].

TABLE 4

number (Table 3)	content of Al ₂ O ₃ , molar parts	Properties of ceramic samples*		
		water absorption, %	apparent density, %	open porosity, %
5.1	0.05	0.00	3.72	0
5.2	0.10	0.00	3.63	0
5.3	0.20	3.71	3.01	15
5.4	0.30	3.98	2.94	26

* Firing temperature 1450°C.

To conclude, it should be noted that corundum ceramics with zero open porosity can be obtained in firing at 1450 – 1550°C by adding to alumina 10 and 5 wt.% glass, respectively, whose composition corresponds to the eutectic of the CaO – B₂O₃ – SiO₂ system with a melting point of 1118°C. The efficiency of flux-forming borosilicate additives depend mainly on their chemical composition and not on the melt structure and can be estimated based on the molar ratios MeO : Al₂O₃ and ψ_B . These relations reflect the chemical factor in sintering of Al₂O₃ according to the liquid-recrystallization mechanism. Taking into account the chemical factor in research and development of ceramic compositions, one can develop energy- and resource-saving technologies.

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